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Intermediates for the Preparation of Ring-Labeled Benzene

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### Authors

Shelberg, W.E.  
Tolbert, B.

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Wesley E. Shelberg and B. M. Tolbert

February 1, 1949

Berkeley, California

INTERMEDIATES FOR THE PREPARATION OF RING-LABELED BENZENE

by

Wesley E. Shelberg\* and B. M. Tolbert

Radiation Laboratory and Department of Chemistry  
University of California, Berkeley, California\*\*

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ABSTRACT

The preparation of radioactive acetylenedicarboxylic acid, for use in the preparation of benzoic acid labeled in the ring with C<sup>14</sup>, by the carbonation of acetylene dimagnesium bromide solutions was examined under various conditions and found to be impractical. Calcium carbide does not yield calcium acetylenedicarboxylate by carbonation in the pressure and temperature ranges of 900-5675 psi and 22-335° C.

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\* Present address: Naval Radiological Defense Laboratory, San Francisco Naval Shipyard, San Francisco, California.

\*\* The work described in this paper was sponsored by the Atomic Energy Commission.

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## INTERMEDIATES FOR THE PREPARATION OF RING-LABELED BENZENE

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Wesley E. Shelberg\* and B. M. Tolbert

Radiation Laboratory and Department of Chemistry,  
University of California, Berkeley, California\*\*

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Methods for the preparation of simple benzene derivatives labeled in the ring with  $C^{14}$  are important, since these derivatives are required for the synthesis of ring-labeled, aromatic natural products. The problem is complicated by the fact that all active starting materials must originate from molecules as simple as carbon dioxide or acetylene and that a satisfactory procedure should involve a minimum number of steps after the one introducing activity. Three reactions which have been used successfully in the preparation of labeled aromatic rings are (a) the dehydration of acetone to yield xylene (1), (b) the dehydrogenation of heptene-1 to yield toluene (2a) and (c) condensation of pyruvic acid to uvitic acid and subsequent decarboxylation to toluene. (2b). Since these methods did not afford good yields of the benzene derivatives, it was decided to further investigate the preparation of ring-labeled compounds.

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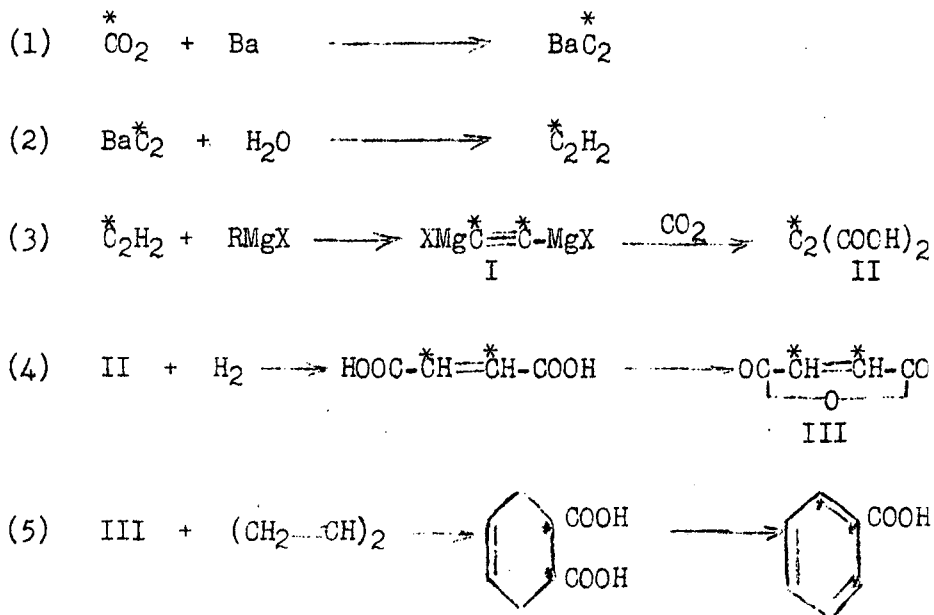
\* Present address: Naval Radiological Defense Laboratory, San Francisco Naval Shipyard, San Francisco, California.

\*\* The work described in this paper was sponsored by the Atomic Energy Commission.

(1) Grosse and Weinhouse, *Science*, 104, 402 (1946).  
(2) a. Wheatcroft, Tolbert and Powell, unpublished work.  
(2) b. Reid, Hughes and Calvin, unpublished work.

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Many of the Diels-Alder condensations (3) yield compounds which are useful intermediates in the preparation of aromatic rings. A series of reactions leading to ring-labeled benzoic acid via a diene synthesis was contemplated:



The preparation and carbonation of acetylene dimagnesium bromide, I, are the critical reactions in this scheme (step (3)) and form the basis of a series of experiments described in this report. Barium carbide may be prepared nearly quantitatively (step (1)) by heating barium and carbon dioxide in a bomb according to the procedure of Arrol and Glascock (4). The manufacture of acetylene from barium carbide (step (2)) and the conversion of acetylenedicarboxylic acid, II, to maleic anhydride, III, (step (4)) should be accomplished in high yield. The reaction between III and butadiene is quantitative (5) (step (5)), and it is believed that  $\Delta^4$ -tetrahydrophthalic

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- (3) Norton, Chem. Rev., 31, 319 (1942).  
 (4) Arrol and Glascock, Nature, 159, 810 (1947).  
 (5) Diels and Alder, Ann., 460, 113 (1928).
-

acid may be converted to benzoic acid in good overall yield. Butadiene also reacts directly with II to give a 44% yield of  $\Delta^{1,4}$ -dihydrophthalic acid (6).

It has long been known that acetylene will form the dimagnesium bromide salt, I, (7) (8) (9) (10) (11). Grignard (11) claimed the formation of acetylenedicarboxylic acid, II, in small yield along with good yields of propionic acid by the carbonation of acetylene monomagnesium bromide containing a small amount of I. Iotsitsch (7) stated that I may be carbonated to II but did not give any yield. However, no conditions were found in the present work whereby it was possible to convert I to II in good yield by the reactions outlined in step (3). Acetylene Grignard solutions were prepared on the 20 mmole scale (a) by using vacuum line techniques (see Experimental section for details and reaction conditions) with reactions between acetylene and hexyl or phenyl magnesium bromide and (b) by using bomb techniques with reactions between acetylene and ethyl magnesium bromide. The former solutions were carbonated on the vacuum line while the latter were carbonated in the bomb. In each case, along with the respective heptanoic, benzoic or propionic acid, a poor or negligible yield of very crude unsaturated acids was obtained. Macro experiments of the flow type in which I was formed by the bubbling of acetylene through ethyl magnesium bromide proved to be impractical since the ratio of the acetylene passing through the solution to that absorbed was 15:1 or greater. The small amounts of unsaturated acids obtained by subsequent carbonation in the flow type experiments were extremely crude. In fact, the yields of unsaturated acids obtained in all of the experiments were too low to be of use in radioactive synthesis, and it was not deemed worthwhile to isolate pure II from the crude reaction products.

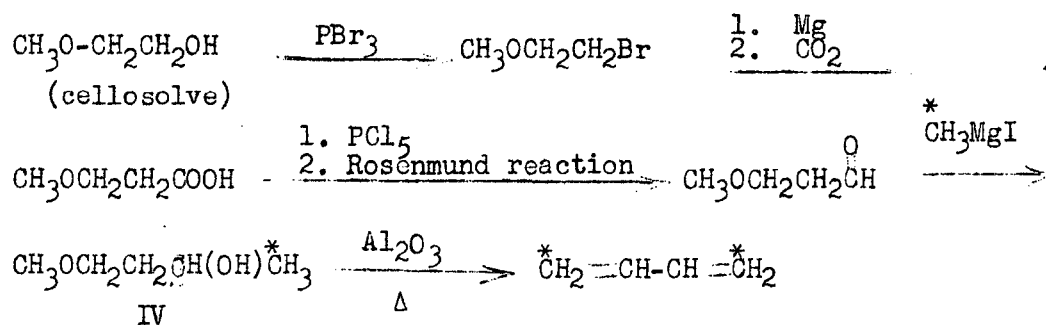
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- (6) Alder and Backendorf, Ber., 71, 2205 (1938).
  - (7) Iotsitsch, Bull. Soc. Chim., 30, 210 (1903).
  - (8) Gauthier, Ann. chim., 16, 289 (1909).
  - (9) Viguier, Ann. chim., 30, 485 (1913).
  - (10) Auwers and Dusterdiek, J. prakt. Chem., 119, 66 (1928).
  - (11) Grignard, Comptes Rendus, 187, 517 (1928).



Collins at the Clinton Laboratories has recently reported (12) the conversion of II to benzoic acid by a series of reactions differing from the above scheme. The reactions are suitable for use with radioactive materials and one of them involves a diene synthesis. Collins has proposed that II be prepared by the preparation and carbonation of I, i.e., the reactions investigated in the present work (step (3)), but he did not report any investigation of these reactions.

The possible formation of calcium acetylenedicarboxylate by the high pressure carbonation of calcium carbide (calcium acetylide) was investigated. The experiments indicated that no reaction occurred between these materials even when the temperature was 335° C and the carbon dioxide pressure was 5675 psi.

Because the preparation of radioactive acetylenedicarboxylic acid by means of step (3) in the above reaction scheme proved to be impractical and the carbonation of calcium carbide fails to give the calcium salt of this acid, it is believed that a more satisfactory approach to the formation of ring-labeled benzoic acid involves the reaction between maleic anhydride and radioactive butadiene. This approach is outlined by step (5) above (disregard asterisks) and the synthesis of radioactive butadiene is contemplated by means of the following reactions:



(12) C. Collins, "Synthesis of Complex Compounds Containing C<sup>14</sup>," Clinton Laboratories Chemistry Division Report CNL-37, page 87.

In order to investigate the conditions required for the conversion of IV to butadiene by means of catalytic de-alcoholation by passing over heated, activated alumina a pilot experiment was performed with the dimethyl ether of 1,3-butanediol. While the single experiment failed to give butadiene under the conditions employed (see Experimental section) it is believed that the reaction merits further investigation. Additional investigations concerning the production of radioactive butadiene were not possible at this time.

#### EXPERIMENTAL

Acetylene: The acetylene used in all the experiments except those of the flow type was generated on the vacuum line from inactive calcium carbide and water.

A two-necked flask containing calcium carbide was fitted with a dropping funnel and was connected to a vacuum manifold through a reflux condenser containing dry ice and acetone. The system was evacuated with house vacuum and the acetylene was generated slowly (cooling) by dropwise addition of water. The acetylene was condensed in a trap immersed in liquid nitrogen and a pressure of approximately 70 cm. was maintained with house vacuum in the system during the gas generation.

The acetylene was then degassed with high vacuum and dried by passing several times through a spiral immersed in dry ice-acetone. The gas was then dried over phosphorus pentoxide in a gas drying bulb and stored in a suitable gas storage vessel.

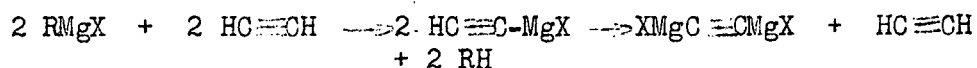
The Carbonation of an Acetylene Grignard Solution Made from Acetylene and n-Hexyl Magnesium Bromide: Isolation of n-Heptanoic Acid: Acetylene di-magnesium bromide has been made by the interaction of acetylene and ethereal ethyl or phenyl magnesium bromide (11); the products are the diGrignard salt and ethane or benzene. The reaction with ethyl magnesium bromide does not lend itself readily to the closed systems used in vacuum techniques because two moles of gaseous ethane are liberated for every mole of diGrignard salt formed. To circumvent this difficulty, hexyl magnesium bromide was used thus producing hexane which is liquid at ordinary temperature and pressure.

One neck of a 250 cc. three-necked, pear-shaped flask was fitted with a vacuum seal stirrer and another with a dry ice-acetone reflux condenser, the top of which was connected with a vacuum gauge and had a stopcock outlet. The third neck was connected via a stopcock to the manifold of a vacuum system. Hexyl magnesium bromide (0.76 m.equiv./ml.) was prepared in the usual manner on the bench top. Fifty-three ml. (40 m.equiv.) of the Grignard solution was transferred to the reaction flask by means of a hypodermic needle; during this operation the flask was flushed with dry nitrogen. The flask was closed, the contents were frozen with liquid nitrogen and the system was evacuated. Twenty mmoles of acetylene was distilled into the reaction vessel which was then closed from the manifold and allowed to warm to room temperature. The vessel was stirred for 30 minutes and, by cooling when it became necessary, it was kept at just below atmospheric pressure at 20° C. The flask was brought to -20° C, opened to a 5 l. bulb of dry carbon dioxide at about one atmosphere pressure and stirred at this temperature (wet ice-acetone bath) until the manifold manometer indicated that no more carbon dioxide was being absorbed. This required about 30 minutes. The complex was then decomposed in the cold with 6 N sulfuric acid and extracted

thoroughly with ether. The ether solution was extracted with 5% aqueous potassium hydroxide, and the combined alkaline portions were acidified with 6 N sulfuric acid. The aqueous portion was extracted with ether, and the ether solution was dried over anhydrous sodium sulfate and evaporated. A crude yield of 4.0 g. (78.4% based on hexyl bromide) of dark, oily n-heptanoic acid was obtained. A rapid distillation gave a colorless sample, b.p., 217-219° C (uncorrected); lit. b.p., 223° C.

The formation of n-heptanoic acid in good yield indicates that the acetylene had formed but little acetylene dimagnesium bromide under the above conditions.

The Carbonation of an Acetylene Grignard Solution Prepared from Acetylene and Phenyl Magnesium Bromide: It is believed that the following series of reactions occur between an alkyl or aryl magnesium halide and acetylene:



It seems that the presence of an excess of RMgX should be beneficial to the formation of the acetylene dimagnesium halide. For this reason, a 100% excess of phenyl magnesium bromide was used in the following procedure.

A three-necked, pear-shaped reaction vessel was fitted with a vacuum seal stirrer, a dropping funnel having a by-pass and a dry ice-acetone reflux condenser having a stopcock outlet and fitted with a vacuum gauge. A solution of 13 g. of bromobenzene in 40 cc. of ether was placed in the dropping funnel and 1.92 g. (80 mmoles) of magnesium plus a crystal of iodine was placed in the flask. The phenyl magnesium bromide was then made in the usual manner, and the system was simultaneously flushed with a slow stream of nitrogen entering at the top of the dropping funnel. Heating was required toward the end of the reaction and a small amount of the magnesium remained unreacted. After completion of this reaction, the dropping funnel

was replaced by a closed stopcock connected to the manifold of the vacuum system. It was estimated that the volume of the reaction system up to the manifold was about 600 cc.

The phenyl magnesium bromide solution was frozen in liquid nitrogen, the reaction vessel was evacuated and 9.3 mmoles of dry acetylene was distilled into the flask. The closed system was allowed to warm up to room temperature and was then placed in a water bath at  $34^{\circ}$  C; the contents were stirred at this temperature for 30 minutes. The temperature of the bath was then raised to  $55^{\circ}$  C and the reaction mixture was stirred for an additional 30 minutes.

The reaction mixture was refrozen in liquid nitrogen, and an additional 11.0 mmoles of acetylene was distilled into the flask. The flask was then stirred for one hour in a water bath at  $30^{\circ}$  C which was the maximum temperature possible without exceeding one atmosphere pressure in the closed systems. The acetylene was added in two portions so that the reaction mixture could be heated at a higher temperature than otherwise would have been possible.

The mixture was cooled to  $-20^{\circ}$  C and opened to a flask of carbon dioxide at 0.75 atmosphere pressure. The mixture was stirred until no more carbon dioxide was absorbed and then decomposed in the cold with 6 N sulfuric acid. The acid solution was extracted with ether and the ether solution was extracted with one 30 cc. portion and two 10 cc. portions of 20% aqueous potassium hydroxide. The combined aqueous solution was acidified to pH 3 with sulfuric acid, and the resulting precipitate was removed by filtration at  $4^{\circ}$  C. A crude yield of 9.2 g. (94.1%) of benzoic acid was obtained, m.p.  $112-115^{\circ}$  C. The benzoic acid did not discharge the color from a dilute solution of bromine in carbon tetrachloride. A recrystallized sample had a m.p. of  $121^{\circ}$  C.

The acidic-aqueous filtrate from the benzoic acid precipitation (which should have contained any acetylenedicarboxylic acid formed in the reaction) was extracted thoroughly with ether and the ether solution was dried with a small amount of anhydrous sodium sulfate. No appreciable amount of residue was obtained upon evaporation of the ether.

The fact that an excellent yield of benzoic acid was obtained indicates that only a negligible amount of the phenyl magnesium bromide could have been converted to acetylene dimagnesium bromide under the above conditions.

The Carbonation of an Acetylene Grignard Solution Formed by the Reaction Between Magnesium and Phenyl Bromide in the Presence of Acetylene: Grig-

nard (11) has reported the preparation of an acetylene Grignard solution by allowing ethereal phenyl bromide and magnesium to react in an atmosphere of acetylene. It was believed that this procedure might afford better results than the one described in the preceding experiment.

A 500 cc. three-necked, pear-shaped flask fitted with a vacuum seal stirrer and a dry ice-acetone reflux condenser having a vacuum gauge and a stopcock outlet was connected to the manifold of a vacuum system through a stopcock connection. The reaction vessel system was flushed with dry nitrogen and the flask was placed in a dry ice-acetone mixture. A mixture of 1.43 g. (60 mmoles) of magnesium, 9.8 g. (62 mmoles) of phenyl bromide, 30 cc. of ether and a crystal of iodine was placed in the flask and solidified with liquid nitrogen before reaction occurred. Then, 14.5 mmoles of acetylene was distilled into the flask.

No reaction occurred when the isolated system was allowed to warm to room temperature, but a reaction started within 15 minutes when the flask was warmed. Grignard formation required about one-half hour and was moderated by cooling whenever necessary to keep the pressure in the system

at or less than atmospheric. When the vigorous reaction ceased, the mixture was heated by a water bath at 40-45° C for one-half hour. Some of the gaseous contents of the system were then stored temporarily in the manifold and the remaining material was stirred for 25 minutes in a water bath at 55-60° C. The entire reaction material was then condensed in the reaction vessel.

The reaction mixture was carbonated with excess carbon dioxide at -20° C and decomposed with 6 N sulfuric acid according to the procedure described in the previous experiment. The acidic mixture was extracted 5 times with liberal portions of ether, and the filtered ether solution was concentrated to a small volume and extracted with one 25 cc. portion and two 10 cc. portions of 20% aqueous potassium hydroxide. The filtered aqueous solution was acidified to pH 3 with sulfuric acid and the precipitated benzoic acid was removed by filtration at 4° C. A dry yield of 4.9 g. (65.3% based on bromobenzene) of benzoic acid was obtained, m.p. 121° C after recrystallization. The crude benzoic acid did not decolorize a dilute solution of bromine in carbon tetrachloride. Evaporation of the ether solution from the alkaline extraction gave 1.6 g. of neutral, oily material which was probably a mixture of bromobenzene and biphenyl.

The acidif filtrate from the benzoic acid filtration was extracted 5 times with 40 cc. portions of ether. The ether was evaporated on a water bath and the reaction product was dried by evacuating the containing flask with high vacuum on the water bath. A yield of 0.14 g. (8.4%, calculated as acetylenedicarboxylic acid and based on acetylene) of dark brown, semi-solid, acidic residue was obtained. It possessed a sharp, irritating odor and decolorized a dilute solution of bromine in carbon tetrachloride.

The crude yield of impure material produced under the above conditions was too low to warrant isolation of any pure acetylenedicarboxylic acid.

The reaction must afford a high yield of crude acidic material if it is to assume practical importance in the reaction schemes contemplated. While the yield was calculated as acetylenedicarboxylic acid, the product was probably a mixture of this acid and propionic acid.

The Closed Bomb Preparation and Carbonation of an Acetylene Grignard Mixture:

The Reaction Between Acetylene and Ethyl Magnesium Bromide:

a. The use of a small bomb at room temperature. It was believed that a heavy layer of ether might have shielded the Grignard reagents from the acetylene in the previous experiments. To circumvent this difficulty it seemed advisable to perform the preparation and carbonation of acetylene dimagnesium bromide on a 20 mmole scale in a stainless steel bomb of 55 ml. capacity with shaking. No gauge was used with the bomb.

Ethyl magnesium bromide of concentration 2.5 m.equiv./cc. was prepared on the bench top by the usual procedure in an atmosphere of nitrogen. Thirty cc. (75 m.equiv.) of the reagent was transferred to the unassembled bomb by means of a hypodermic needle; during this operation the bomb was flushed with a stream of dry nitrogen. The bomb was fitted with its valve, connected to the manifold of a vacuum system and surrounded by a Dewar of liquid nitrogen. After the contents of the bomb had solidified, it was evacuated and 20 mmoles of acetylene was distilled into the bomb. The bomb was warmed to room temperature and was shaken mechanically for 3 hours. The contents were then resolidified with liquid nitrogen and 98 mmoles of carbon dioxide was distilled into the bomb. It was then warmed to  $-20^{\circ}$  C and shaken mechanically for 55 minutes with intermittent cooling in a wet-ice-acetone bath.

When the bomb was opened it appeared as though a crust had formed at the surface of the Grignard complex. The contents were decomposed in the cold with 6 N sulfuric acid, and the solution was made 6 N by the addition



of the calculated quantity of concentrated sulfuric acid. The acidic solution was extracted with five 150 cc. portions of ether and the combined ether solutions were filtered and evaporated on the water bath. The product was dried and freed from propionic acid by heating it on the water bath under high vacuum. A 0.30 g. yield (13.1% calculated as acetylenedicarboxylic acid and based on acetylene) of black, tarry residue was obtained. It possessed an irritating odor and decolorized a dilute solution of bromine in carbon tetrachloride.

The yield of crude acidic material formed under the above conditions was too low to be of any practical importance to the present work and, therefore, no attempt was made to isolate pure acetylenedicarboxylic acid. Probably a mixture of acetylenedicarboxylic and propiolic acids was formed.

b. The use of a 300 ml. bomb at room temperature. Because it was feared that the crust which had formed on top of the Grignard solution during the carbonation in part a might have prevented complete carbonation, an identical experiment was performed with a larger (300 ml.) bomb. A durable, thick crust might form in a small, narrow bomb, but this should not be possible in a large wide bomb. The same quantities of material as in part a yielded 1.3 g. (56.5%, calculated as acetylenedicarboxylic acid and based on acetylene) of dark, semi-solid acidic material having an irritating odor. A test with bromine in carbon tetrachloride indicated that it was unsaturated. The yield was not high enough for practical purposes.

c. The use of a 300 ml. bomb and a temperature of 50-60° C. An experiment similar to b above was performed with the exception that the mixture of acetylene and ethereal ethyl magnesium bromide was shaken for 2 hours at 50-60° C. The carbonation was performed at room temperature. A 0.48 g.

yield (20.8% as acetylenedicarboxylic acid and based on acetylene) of acidic product was obtained similar to the material isolated in part b. Again, the yield was not good enough to warrant isolation of any pure acetylenedicarboxylic acid.

The Carbonation of Acetylene Dimagnesium Bromide:

a. Carbonation without the use of a solvent. The usual method for the preparation of acetylene dimagnesium bromide consists of bubbling acetylene through ethereal ethyl magnesium bromide until the acetylene Grignard separates as a dark, oily layer (9). Since the closed systems used in vacuum line techniques seemed unpromising in the preparation of acetylenedicarboxylic acid, it was decided to try this flow system. In order for a flow system to be practical with radioactive acetylene, at least 1 volume of acetylene must be converted to the diGrignard for every 4-8 volumes passing through the ethyl magnesium bromide solution. This condition was tested by the use of macro quantities of acetylene.

Acetylene from a commercial cylinder was passed through 3 sulfuric acid traps, an acidic sodium dichromate solution, an acidic cupric nitrate solution, a wet-test gas meter, a tube 1 meter long of potassium hydroxide pellets, 3 Drierite tubes each 1 meter long, an Ascarite tube 1 meter long, a 250 cc. two-necked, pear-shaped reaction vessel and a combination Drierite-Ascarite tube of 1 meter length. The acetylene inlet tube of the reaction vessel reached nearly to the bottom of the flask; the vessel contained a solution of 40 m.equiv. of ethyl magnesium bromide in 30 ml. of ether. This Grignard had been prepared in a separate apparatus and was transferred to the reaction vessel by means of a hypodermic needle in an atmosphere of nitrogen. The acetylene was bubbled through very slowly and very shortly insoluble, oily acetylene dimagnesium bromide precipitated.

After 0.162 mole of acetylene had passed through the reaction vessel, the gas cylinder was closed and a vigorous stream of dry carbon dioxide was introduced through the inlet tube of the reaction vessel for one-half hour at  $-20^{\circ}$  C, and then for 1-1/2 hour at room temperature. Additional ether was added when necessary. The extremely viscous reaction mixture was decomposed in the cold with 6 N sulfuric acid and then made 6 N with concentrated sulfuric acid. The acidic reaction mixture was extracted with ten 100 cc. portions of ether and the combined ether portions were evaporated on the water bath. The residue was freed from water and propionic acid by heating on the water bath under vacuum. A yield of 0.8 g. of dark brown, gummy acidic material was obtained. It possessed a very irritating odor and decolorized a dilute solution of bromine in carbon tetrachloride. On the basis that the entire yield was acetylenedicarboxylic acid, 23.1 volumes of acetylene passed through the reaction vessel for each volume retained by the ethyl magnesium bromide. This experiment indicated that the flow method would be impractical with the use of radioactive acetylene. No attempt was made to isolate pure acetylenedicarboxylic acid.

b. Carbonation with the use of a special solvent. In order to be certain that the poor yield obtained in part a was not caused by incomplete carbonation of the extremely viscous acetylene dimagnesium bromide, a similar experiment was performed in which diphenyl ether was used as a solvent for the acetylene Grignard. While the acetylene Grignard was not completely soluble in the diphenyl ether, it appeared to be the most suitable solvent. The diphenyl ether was added after the acetylene Grignard had been formed and the carbonation was performed at room temperature. The acidified reaction mixture was extracted with ether and the ether solution was extracted with 5% aqueous potassium hydroxide. The alkaline solution was acidified to

6 N with sulfuric acid. The acidic material was isolated from this solution according to the procedure outlined in part a.

From 40 m.equiv. of ethyl magnesium bromide and 0.123 mole of acetylene was obtained 0.9 g. of acidic product similar to that obtained in part a. On the basis that the yield was acetylenedicarboxylic acid, 15.5 volumes of gas passed through the reaction mixture for every volume absorbed. This result substantiates the conclusions reached in part a.

The Attempted Carbonation of Calcium Acetylide:

a. The use of a 2660 psi pressure. Twenty-five g. of powdered calcium carbide was placed in a 300 cc. hydrogenation bomb, and the bomb was connected to a carbon dioxide cylinder and filled with gas at a pressure of 900 psi. The bomb was then placed in a shaker and heated, and a record of the pressure within the bomb at various temperatures was kept. A plot of temperature vs. pressure gave a straight line indicating that Charles' law was being obeyed and that no reaction was occurring. Had a reaction started to occur at any temperature, the pressure would not have increased at a constant rate as the temperature increased. The following data were obtained:

<u>Temp. (° C)</u>	<u>Pressure (lbs./in.<sup>2</sup>)</u>
22	900
55	1200
75	1300
100	1500
130	1640
150	1740
198	2000
250	2220
295	2450
335	2640
344	2660

b. The use of 5675 psi pressure. The experiment in part a was repeated with the exception that 10 g. of calcium carbide was used and the bomb was filled with approximately twice as much carbon dioxide. The result was similar to that obtained in part a and the following data were collected.

<u>Temp. (° C)</u>	<u>Pressure (lbs./in.<sup>2</sup>)</u>
22	900
50	1450
88	2100
100	2250
150	2950
205	3750
246	4300
295	5125
335	5675

1,3-Butanediol Dimethyl Ether: (13) A 2 l. three-necked round bottomed flask was fitted with a tight fitting rubber seal stirrer, a dropping funnel and a reflux condenser, the top of which was connected to a liquid nitrogen trap connected to a vacuum pump. To a solution of 114 g. of 95% sodium methoxide in 400 cc. of methanol was added 90 g. of Eastman 1,3-butanediol. The mixture was evaporated under vacuum and the last traces of methanol were removed by heating under vacuum in an oil bath at 150° C. Ether was added to the salt in the flask and 125 cc. of dimethyl sulfate was added dropwise from the separating funnel with stirring. After the addition was completed the mixture was refluxed with stirring on the steam bath for 10 hours. Water was added to the flask and the mixture was stirred for 4 hours.

The mixture was extracted with ether and the ether was removed by distillation; the material boiling over 45° C was allowed to stand overnight with 200 cc. of 10% aqueous potassium hydroxide. This mixture was extracted

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(13) Baker and Field, J. Chem. Soc., (1932), p. 90; the dimethyl ether of 1,3-propanediol.

with ether and the ether solution was washed 10 times with water (to insure removal of glycol and glycol monomethyl ether) and then with saturated salt solution. The ether solution was dried with anhydrous sodium sulfate and the ether was evaporated. The oily residue was allowed to stand for 1 hour over sodium. The oil distilled as a colorless, fragrant liquid from a modified Claisen flask, b.p., 104-106° C; a 4.5 g. yield of 1,3-butanediol dimethyl ether was obtained.

The Attempted De-alcoholation of the Dimethyl Ether of 1,3-Butanediol to Butadiene: Two and two-tenths g. of the dimethyl ether of 1,3-butanediol was passed through a vertical column of activated alumina at 485° C along with a slow stream of dry nitrogen. The alumina (Alorco, Aluminum Company of America) was of mesh 12-24 and F-4 in quality and formed a column 12" long in a tube of 0.9 cm. diameter. The ether was admitted to the top of the column in a dropwise manner by means of a separatory funnel and 40 minutes were required to complete the addition.

The reaction products were led through a 55 cc. high pressure bomb immersed in a dry ice-acetone bath (-80° C) which served to trap condensable products. The outlet gases were then led through a spiral at -80° C to ensure complete condensation of condensable materials. After the reaction was completed, the spiral was warmed to room temperature and the small amount of liquid it contained was transferred back into the bomb with a slow stream of nitrogen.

A mixture of 1.9 g. of maleic anhydride in 10 cc. of benzene was added to the bomb, and the closed bomb was allowed to remain at room temperature overnight. It was then heated at 100° C for 5 hours. Crystallization of the reaction product from ligroin allowed the isolation of the unreacted maleic anhydride.

The combined reaction product was heated with a dilute solution of potassium hydroxide on the steam bath for 2 hours. Acidification and cooling did not produce any  $\Delta^4$ -tetrahydrophthalic acid.

Polymerization with the formation of some higher boiling oily material occurred during this experiment.

#### SUMMARY

The preparation of radioactive acetylenedicarboxylic acid, for use in the preparation of benzoic acid labeled in the ring with  $C^{14}$ , by the carbonation of acetylene dimagnesium bromide solutions was examined under various conditions and found to be impractical. Calcium carbide does not yield calcium acetylenedicarboxylate by carbonation in the pressure and temperature ranges of 900-5675 psi and 22-335° C.